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Archaeal and bacterial H-GDGTs are abundant in peat and their relative abundance is positively correlated with temperature

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Abstract

Glycerol monoalkyl glycerol tetraether lipids (GMGTs; also called 'H-GDGTs') differ from the more commonly studied glycerol dialkyl glycerol tetraether (GDGTs) in that they have an additional covalent bond that links the two alkyl chains. Six different archaeal isoprenoidal H-GDGTs (H-*iso*GDGTs) and one branched H-GDGT (H-*br*GDGT), presumably produced by bacteria, have previously been found. However, the function of H-GDGTs in both domains of life is unknown. It is thought that the formation of this additional covalent bond results in enhanced membrane stability, accounting for the high abundance of H-GDGTs in extreme environments such as geothermal settings, but so far there has been little evidence to support this hypothesis.

Here we report the distribution of H-GDGTs in a global peat database ($n = 471$) with a broad range in mean annual air temperature (MAAT) and pH. This is the first finding of H-GDGTs in soils (specifically, peat), highlighting that H-GDGTs are widespread in mesophilic settings. In addition, we report the presence of two new H-*br*GDGTs with one (H-1034) and two (H-1048) additional methyl groups, respectively. Our results suggest that the relative abundance of both bacterial and archaeal H-GDGTs compared to regular GDGTs is related to temperature with the highest relative abundance of H-GDGTs in tropical peats. Although other factors besides temperature likely also play a role, these results do support the hypothesis that H-GDGTs are an adaptation to temperature to maintain membrane stability. The observation that both bacterial and archaeal membrane lipids respond to temperature indicates the same adaption across the lipid divide between these two domains of life, suggesting parallel or convergent evolution (potentially facilitated by lateral gene transfer).

Keywords: GMGT; H-GDGT; Membrane lipid; Peat; Global; Temperature

1. INTRODUCTION

Glycerol dialkyl glycerol tetraether (GDGTs) are membrane-spanning lipids and have been identified in a wide range of environmental settings (see review by Schouten et al., 2013). Isoprenoidal GDGTs (*iso*GDGTs) were first identified in extremophilic archaea (De Rosa et al., 1977; De Rosa and Gambacorta, 1988), but during the last two decades it became apparent that *iso*GDGTs are produced by a wide range of archaea and are ubiquitous in natural settings (Pearson and Ingalls, 2013; Schouten et al., 2000, 2013). So far *iso*GDGTs with between 0 and 8 cyclopentane moieties have been identified, although *iso*GDGTs with more than 4 cyclopentane moieties have only been found in extreme settings such as thermal hot springs and cultures of extremophiles (Schouten et al., 2013). In addition to *iso*GDGTs, more recent work identified non-isoprenoidal branched GDGTs (*br*GDGTs) in natural samples, with their structure and stereochemistry

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indicating a bacterial origin (Sinninghe Damsté et al., 2000, 2011; Weijers et al., 2006a). *br*GDGTs are ubiquitous in natural settings, especially mineral soils and peat (De Jonge et al., 2013; Naafs et al., 2017b; Weijers et al., 2006b), but also appear to be produced in riverine and lacustrine settings (De Jonge et al., 2014b; Weber et al., 2015) and within the marine water column (Liu et al., 2014; Xie et al., 2014). Although the exact source organism of *br*GDGTs is still unknown, the ability to produce GDGTs does not appear to be widespread and likely is restricted to acidobacteria (Sinninghe Damsté et al., 2014, 2011). *br*GDGTs can have between 0 and 2 cyclopentane rings as well as between 0 and 2 additional methyl groups, located at either the C-5 or C-6 position (De Jonge et al., 2013; Weijers et al., 2006a).

Four decades of culture experiments, mesocosm experiments, and sediment data from thermal hot springs, lakes, and the ocean show that the degree of cyclization of *iso*GDGTs is correlated with environmental factors such as temperature and pH (Dang et al., 2016; De Rosa et al., 1980; Elling et al., 2015; Kim et al., 2010; Pearson et al., 2008; Powers et al., 2010; Qin et al., 2015; Schouten et al., 2007, 2002, 2013; Ward et al., 1985; Wuchter et al., 2004). Although there is currently no culture data available for *br*GDGTs, observations from natural samples such as mineral soils, peat, and lake sediments indicate that their distribution also depends on environmental factors such as temperature and pH (De Jonge et al., 2014a; Loomis et al., 2014; Naafs et al., 2017b; Weijers et al., 2007). The correlation with pH is similar for *iso*GDGTs and *br*GDGTs, with an increase in cyclization at lower pH. However, the correlation with temperature is different between the two compound classes: archaea increase the degree of cyclization of *iso*GDGTs at higher temperature, whereas the distribution of bacterial *br*GDGTs in natural archives changes in the degree of methylation, not the degree of cyclization, when soils of different climatic zones are compared. Whether this is related to changes in the source organism's *br*GDGT distribution or due to changes in the bacterial community composition is currently unclear.

In addition to the commonly reported regular *iso*GDGTs and *br*GDGTs (Fig. 1), there is a rapidly expanding range of additional GDGTs reported in natural samples (e.g., Liu et al., 2012). One of these are the glycerol monoalkyl glycerol tetraether lipid group (GMGTs; also called 'H-GDGTs' even though they are not strictly dialkyl) that has an extra covalent bond between the two alkyl chains (Fig. 1). Isoprenoidal H-GDGTs (H-*iso*GDGTs) were first identified in cultures of extremophilic *Euryarchaeota* and *Crenarchaeota* (Knappy et al., 2011; Liu et al., 2012; Morii et al., 1998; Schouten et al., 2008a; Sugai et al., 2004) and H-*iso*GDGTs with up to six cyclopentane rings have now also been reported in extreme settings such as hydrothermal vent systems and thermal hot springs (Jaeschke et al., 2012; Jia et al., 2014; Pan et al., 2016). Intriguingly, H-*iso*GDGTs have also been found in marine and lake sediments, suggesting that these compounds are also produced by (unknown) mesophilic archaea (Liu et al., 2012; Pan et al., 2016; Schouten et al., 2008b). So far H-*iso*GDGTs have not been reported in mineral soils or peat and this observation has been used to suggest that marine archaea are the main source of these compounds (Schouten et al., 2008b).

So far one acyclic tetramethylated H-*br*GDGT has been identified in natural samples, tentatively labeled H-1020 (Liu et al., 2012). Although the precise structure of this compound is unknown, the covalent bond is thought to be at the same position as in H-*iso*GDGTs, i.e. in the middle of the alkyl chain (Liu et al., 2012). This H-*br*GDGT is rarely reported and has only been found in a few marine sediments (Liu et al., 2012) and within the oxygen minimum zone of the eastern tropical Pacific (Xie et al., 2014). So far H-*br*GDGTs have not been reported in soils and H-*br*GDGTs with additional methyl groups and/or cyclopentane moieties have not been identified.

Interestingly, both H-*iso*GDGTs and H-*br*GDGT were recently identified in a manganese carbonate ($MnCO_3$) deposit from the Jurassic, suggesting that these compounds are preserved on geological times scales (Bauersachs and Schwark, 2016). However, despite their widespread occurrence and apparent preservation in the geological record, the function of H-GDGTs in bacteria and archaea is currently unknown. Knappy et al. (2011) suggest that H-*iso*GDGTs are biosynthetically derived from regular *iso*GDGTs. The general hypothesis is that linking the two alkyl chains in tetraethers leads to increased membrane stability and it is thus expected that there is an increase in the abundance of H-GDGTs at higher growth temperature. Indeed, Sollich et al. (2017) have recently shown that the relative abundance of H-*iso*GDGTs was positively correlated with temperature in marine sediments across different thermal gradients. However, besides that study there is very little evidence that suggests that the occurrence of H-*iso*GDGTs, let alone H-*br*GDGTs, is related to temperature. Here we investigate the occurrence of H-GDGTs in a global peat database to assess whether H-GDGTs are abundant in terrestrial settings and to determine if there is a correlation between the occurrence of H-GDGTs in (terrestrial) mesophilic settings and environmental factors (e.g. temperature, pH, altitude).

2. MATERIAL AND METHODS

We used the global T-GRES peat database (Naafs et al., 2017b) that consists of 471 samples from 96 different peatlands from around the world. All samples were taken from the top 1 m and typically represent several decades to centuries of accumulation. Samples were taken from both the acrotelm (typically above the water table and oxic) and catotelm (below the water table and anoxic). The database consists of peats from every climatic zone and continent (besides Antarctica) with a temperature and pH range from −8 to 27 °C and 3 to 8, respectively. Samples were obtained from altitudes ranging from 0 to 3500 m above sea level. Details on sample preparation and GDGT analysis are given in Naafs et al. (2017b). Briefly, (H-)GDGTs were analyzed by high performance liquid chromatography/atmospheric pressure chemical ionisation – mass spectrometry (HPLC/APCI-MS) using a ThermoFisher Scientific Accela

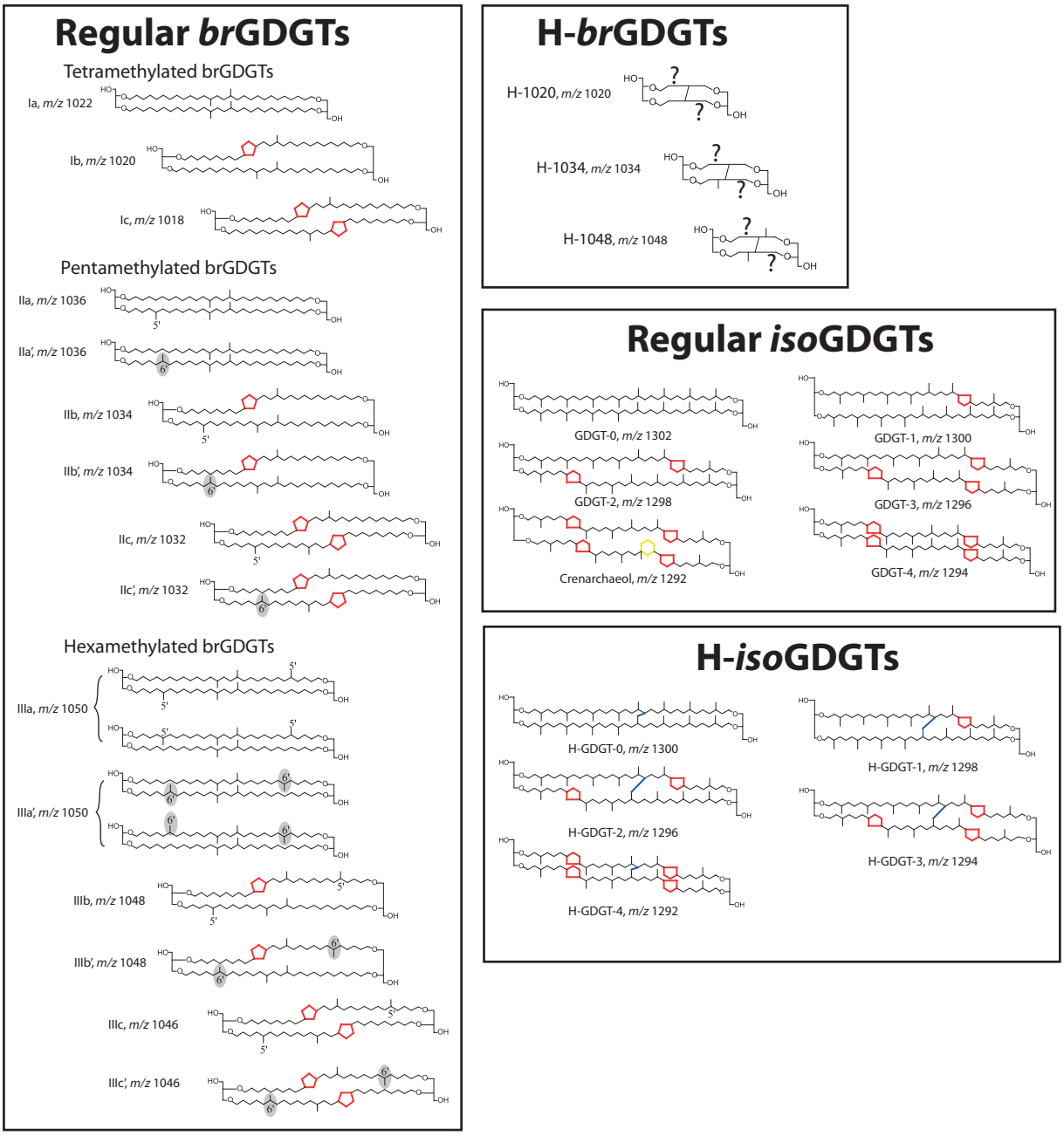

Fig. 1. Structures of GDGTs discussed in the text. Note that the exact location of the covalent bond between the two alkyl chains in both H-*iso*GDGTs and H-*br*GDGTs is unknown.

Quantum Access triplequadrupole mass spectrometer. Normal phase separation was achieved using two ultra-high performance liquid chromatography silica columns, following Hopmans et al. (2016). Analyses were performed using selective ion monitoring mode (SIM) to increase sensitivity and reproducibility (*m/z* 1302, 1300, 1298, 1296, 1294, 1292, 1050, 1048, 1046, 1036, 1034, 1032, 1022, 1020, 1018, 744, and 653). For a number of ombrotrophic tropical peats we also scanned for *m/z* 1290 and 1288. H-*iso*GDGTs and H-*br*GDGTs (Figs. 1 and 2) were identified based on relative retention times and mass spectra (Jia et al., 2014; Liu et al., 2012; Schouten et al., 2008a). Novel H-*br*GDGTs were identified based on HPLC/APCI-MS^2 spectra. For this purpose the triplequadrupole MS scanned for *m/z* 200–1100 with parent ions *m/z* 1022, 1020, 1034, and 1048, using a collision energy of 30 V, scan time of 0.45 s, and collision gas pressure of 5 mTorr.

The GDGT distribution was compared to MAAT and *in situ* pH as given in Naafs et al. (2017b). The relative abundance of H-*iso*GDGTs over regular *iso*GDGTs with 0 to 3 cyclopentane moieties (H-*iso*GDGT-0, -1, -2, -3) and H-*br*GDGTs over regular *br*GDGTs with up to two

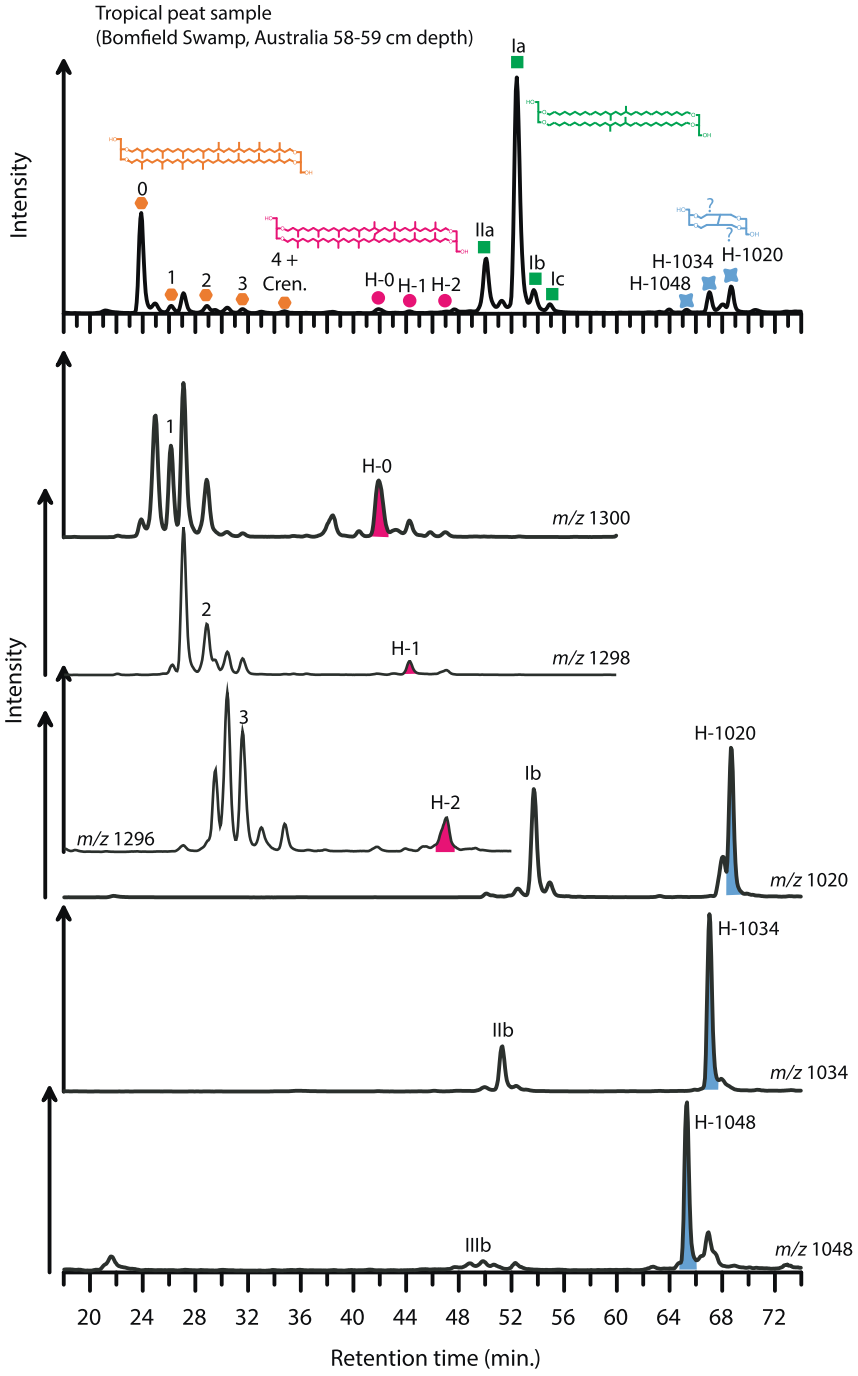

Fig. 2. HPLC-APCI-MS base peak chromatogram (top) and mass chromatograms of an Australian tropical peat (Bomfield swamp peatland, 58–59 cm depth), highlighting the elution pattern of (H-)GDGTs.

additional methyl groups (H-*br*DGT-Ia, -IIa, -IIIa) was calculated using;

$$\text{H}-\textit{iso}\text{GDGT}\ (\%) = 100 \times \frac{\sum_{3}^{0}\text{H}-\textit{iso}\text{GDGTs}}{\left(\sum_{3}^{0}\text{H}-\textit{iso}\text{GDGTs} + \sum_{3}^{0}\textit{iso}\text{GDGTs}\right)} \quad (1)$$

$$\text{H}-\textit{br}\text{GDGT}\ (\%) = 100 \times \frac{\sum_{\text{IIIa}}^{\text{Ia}}\text{H}-\textit{br}\text{GDGTs}}{\left(\sum_{\text{IIIa}}^{\text{Ia}}\text{H}-\textit{br}\text{GDGTs} + \sum_{\text{IIIa}}^{\text{Ia}}\textit{br}\text{GDGTs}\right)} \quad (2)$$

Note that the relative abundance of H-*iso*GDGTs was calculated using GDGT-0 in the denominator. This compound is produced by a wide range of archaea and is very abundant in peat (e.g., Schouten et al., 2013; Weijers et al., 2004), whereas H-*iso*GDGTs have only been found in a few strains (e.g., Knappy et al., 2011). It is not known whether the ability to produce H-*br*GDGTs is widespread among *br*GDGT-producing bacteria, but the inclusion of H-*iso*GDGT-0 in Eq. (1) likely leads to the overall lower abundance of H-*iso*GDGTs compared to H-*br*GDGTs.

The degree of methylation of both regular and H-*br*GDGTs without cyclopentane moieties (acyclic) was

calculated using a modified methylation of branched tetraether index that includes only *br*GDGTs without cyclopentane moieties;

$$\mathrm{MBT}_{\mathrm{acyclic}} = \frac{br\mathrm{GDGT-Ia}}{(br\mathrm{GDGT-Ia} + br\mathrm{GDGT-IIa} + br\mathrm{GDGT-IIa'} + br\mathrm{GDGT-IIa} + br\mathrm{GDGT-IIIa'})} \quad (3)$$

$$\mathrm{H-MBT}_{\mathrm{acyclic}} = \frac{\mathrm{H-}br\mathrm{GDGT-Ia}}{(\mathrm{H-}br\mathrm{GDGT-Ia} + \mathrm{H-}br\mathrm{GDGT-IIa} + \mathrm{H-}br\mathrm{GDGT-IIIa})} \quad (4)$$

The degree of cyclization of both regular and H-*iso*GDGTs with up to 3 cyclopentane moieties was calculated using the ring index;

$$\text{Ring index} = \frac{(iso\mathrm{GDGT-1} + (2 \times iso\mathrm{GDGT-2}) + (3 \times iso\mathrm{GDGT-3}))}{(iso\mathrm{GDGT-0} + iso\mathrm{GDGT-1} + iso\mathrm{GDGT-2} + iso\mathrm{GDGT-3})} \quad (5)$$

$$\text{H-Ring index} = \frac{(\mathrm{H-}iso\mathrm{GDGT-1} + (2 \times \mathrm{H-}iso\mathrm{GDGT-2}) + (3 \times \mathrm{H-}iso\mathrm{GDGT-3}))}{(\mathrm{H-}iso\mathrm{GDGT-0} + \mathrm{H-}iso\mathrm{GDGT-1} + \mathrm{H-}iso\mathrm{GDGT-2} + \mathrm{H-}iso\mathrm{GDGT-3})} \quad (6)$$

3. RESULTS

H-*iso*GDGTs were detected in 237 out of the 471 samples analyzed. H-*iso*GDGTs with between zero and four cyclopentane moieties were present (Figs. 1 and 2). In the majority of samples H-*iso*GDGT-0 was the most abundant isoprenoidal H-GDGT, comprising 31–100% of the total H-*iso*GDGT distribution. H-*iso*GDGT-4 was only present at trace level in a few samples and H-*iso*GDGTs with more than four cyclopentane moieties were not detected.

In general H-*br*GDGTs were more abundant than H-*iso*GDGTs and were present in 386 out of the 471 samples analyzed. Besides the known H-*br*GDGT (H-1020), which comprised 0–100% of the total H-*br*GDGT distribution, some samples also contained compounds with dominant peaks at *m*/*z* 1034 and 1048 that eluted ~1.5 and 3 min before H-1020, respectively (Fig. 2). This elution pattern is identical to that seen for the regular *br*GDGTs with an increase in methylation causing the compound to elute slightly earlier. The HPLC/APCI-MS^2 spectrum of the 1034 peak (Fig. 3c) is similar to that obtained for H-1020 (Fig. 3b) with prominent ions from losses up to 184 daltons (Da) due to characteristic water losses (−18 Da) and glycerol losses (−74 Da) (Fig. 3a). Crucially, we do not observe the loss on the alkyl chain typically observed in regular *br*GDGTs (Fig. 3a). The same fragmentation pattern was observed by Liu et al. (2012) for H-1020 and for the H-*iso*GDGTs (Knappy et al., 2011). We therefore tentatively identify these earlier eluting compounds as penta- (H-1034) and hexamethylated H-*br*GDGTs (H-1048). Whilst this is likely related to changes in the degree of methylation, this could also be attributed to an increase in chain length. Regardless, our results extend the known range of H-*br*GDGT.

On average the abundance of H-GDGTs was correlated with the abundance of regular GDGTs, but H-GDGTs were never more abundant than their regular counterpart (Fig. 4). Based on changes in LC-MS signal intensity, the concentration of H-GDGTs is higher at depth compared to the surface of peat. This is similar to that seen for regular *br*- and *iso*GDGTs (e.g., Weijers et al., 2004), suggesting particularly high production by anaerobic organisms.

The relative abundance of both H-*iso*GDGTs and H-*br*GDGTs over regular GDGTs (Eqs. (1) and (2)) is higher in tropical peat compared to mid- and high-latitude peats (Fig. 5a and b). The highest relative abundance of H-*iso*GDGTs (11%) was observed within a tropical peat sample from Peru. The highest relative abundance of H-*br*GDGTs (26%) was observed in a tropical peat sample from Indonesia. We observe no clear correlation between the relative abundance of H-GDGTs and pH (Fig. 5c and d) or with altitude (Fig. 5e and f). Some, but crucially not all, downcore peat profiles indicate that the relative abundance of both H-*iso*GDGTs and H-*br*GDGTs over their regular counterpart (Eqs. (1) and (2)) increases with depth (Fig. 6). The degree of methylation of H-*br*GDGTs (Eq. (4)) is linearly correlated (Fig. 7a) with the degree of methylation of *br*GDGTs (Eq. (3)). In contrast, the degree of cyclization of H-*iso*GDGTs is not correlated with that of *iso*GDGTs (Fig. 7b).

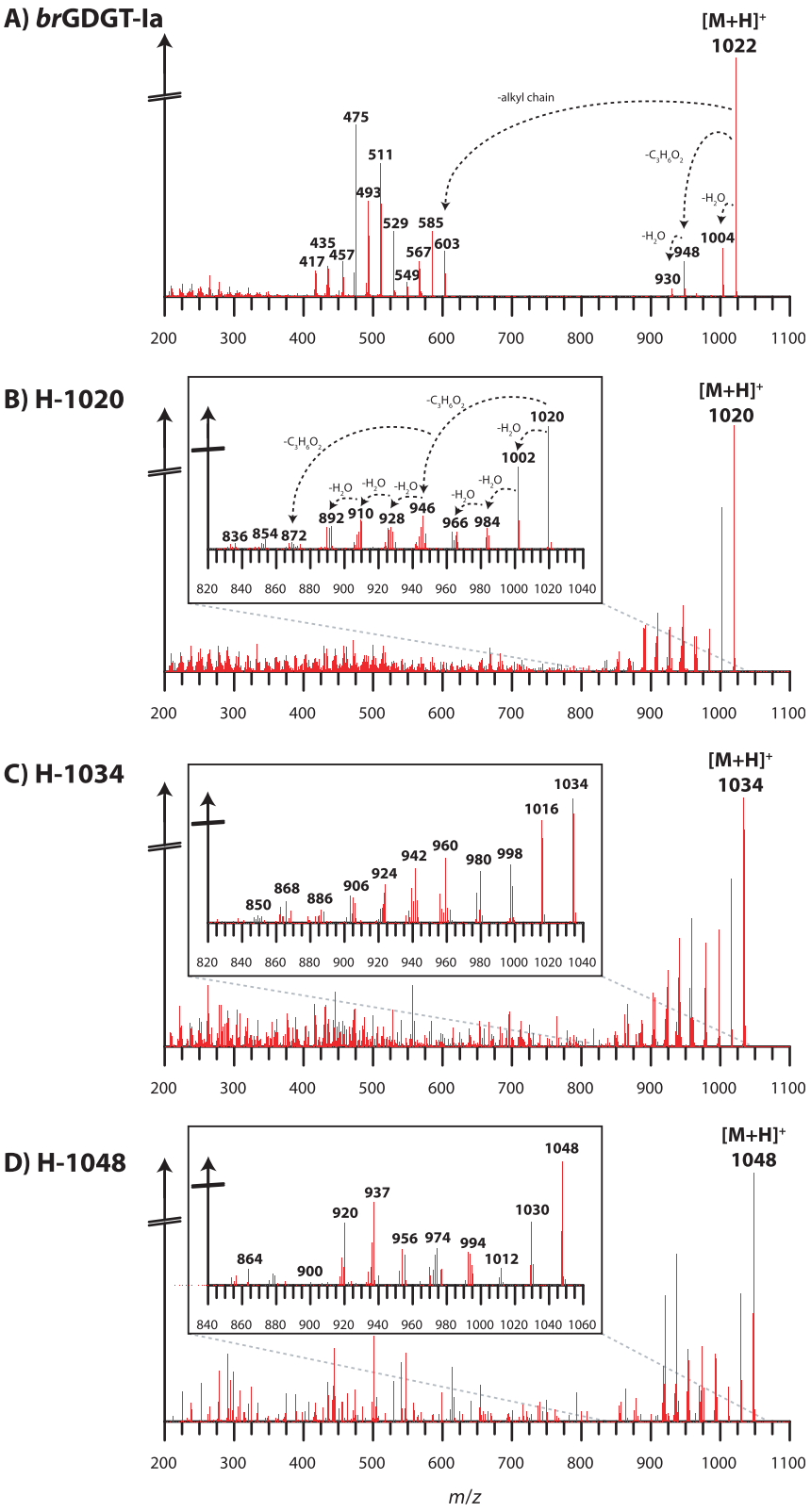

Fig. 3. HPLC-APCI/MS^2 spectra of (A) brGDGT-Ia, (B) H-1020, (C) H-1034, and (D) H-1048.

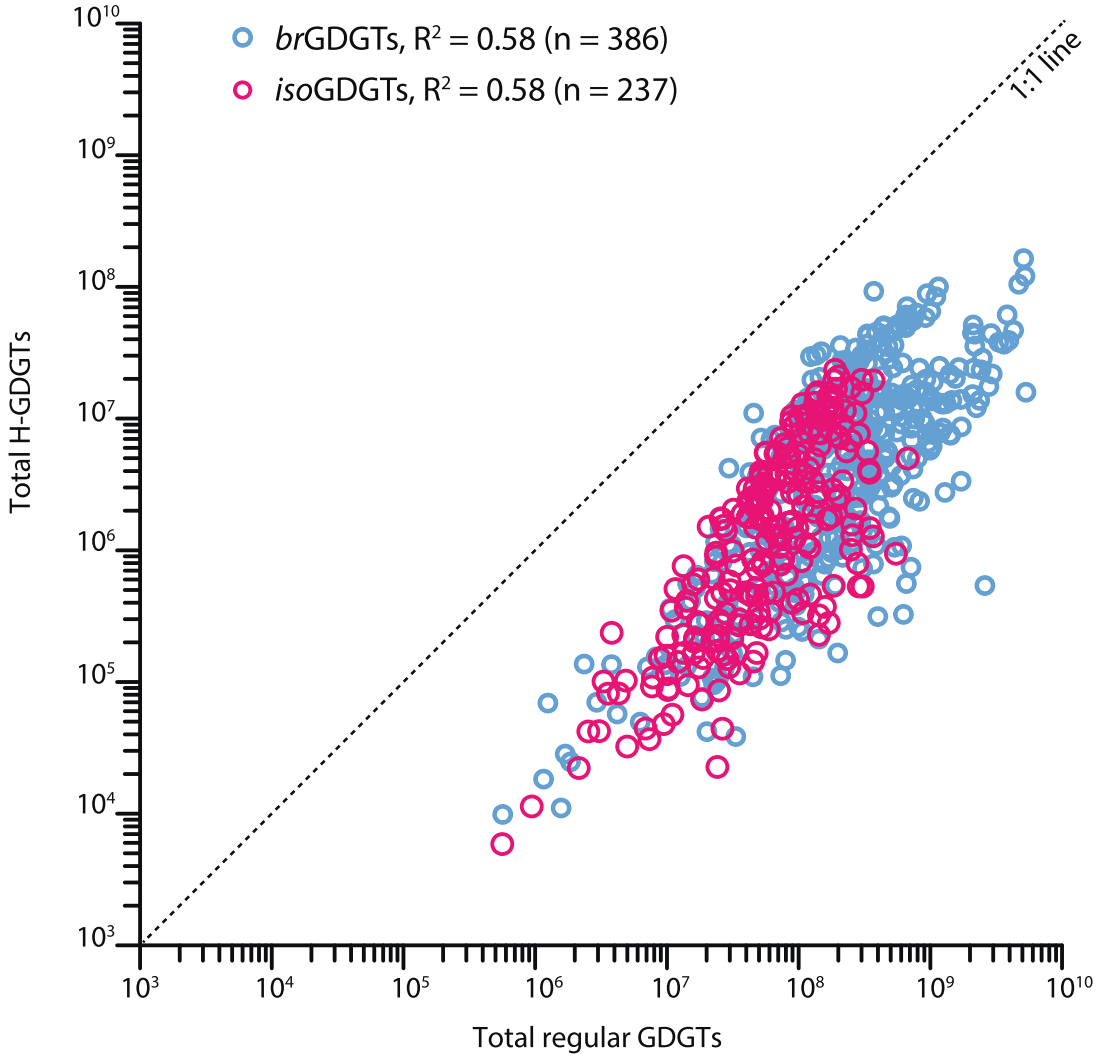

Fig. 4. Comparison between the signal intensity of the regular GDGTs versus H-GDGTs in the global peat dataset.

4. DISCUSSION

4.1. Presence of H-GDGTs in peat

So far H-*iso*GDGTs have only been found in cultures of extremophilic archaea and the source of H-*br*GDGTs is unknown. In natural archives, H-GDGTs have been predominantly identified in marine settings, and, to the best of our knowledge, this is the first reported occurrence of H-GDGTs in peat. Our results thus add to the growing body of work (e.g., Liu et al., 2012; Schouten et al., 2008b) indicating that H-GDGTs are also produced by mesophilic archaea and bacteria and are ubiquitous in both marine and terrestrial settings.

The identification of H-1034 and H-1048 in peat extends the known range of H-*br*GDGTs. We did not detect H-*br*GDGTs with cyclopentane rings (e.g. *m*/*z* 1018, 1032), even in alkaline peats with a high abundance of regular *br*GDGT with cyclopentane moieties such as *br*GDGT-Ib/c and –IIb/c. We speculate that for *br*GDGTs the formation of cyclopentane rings close to the middle of the alkyl chain prevents the formation of a covalent bond between the two alkyl chains. For *iso*GDGTs the cyclopentane rings do not occur close to the middle of the alkyl chains, allowing for H-*iso*GDGTs with cyclopentane rings. In this context, future studies should explore whether newly identified S-GDGTs (Liu et al., 2016b), which contain a cyclohexane ring in the middle of one or both of the alkyl-chains, have an H-counterpart.

The correlation between the abundance of H-GDGTs versus regular GDGTs (Fig. 4) suggests that the controls on the occurrence of regular and H-GDGTs in peat (e.g. abundance of source organisms and/or rate of diagenesis) are similar. The correlation between the abundance of H-GDGTs versus regular GDGTs could result from a precursor/product relationship and lends further support for the hypothesis of Knappy et al. (2011) that H-*iso*GDGTs are biosynthetically derived from regular *iso*GDGTs, although this hypothesis requires further testing.

4.2. Correlation with pH

We find no evidence for a correlation between the relative abundance of either H-*iso*GDGTs or H-*br*GDGTs

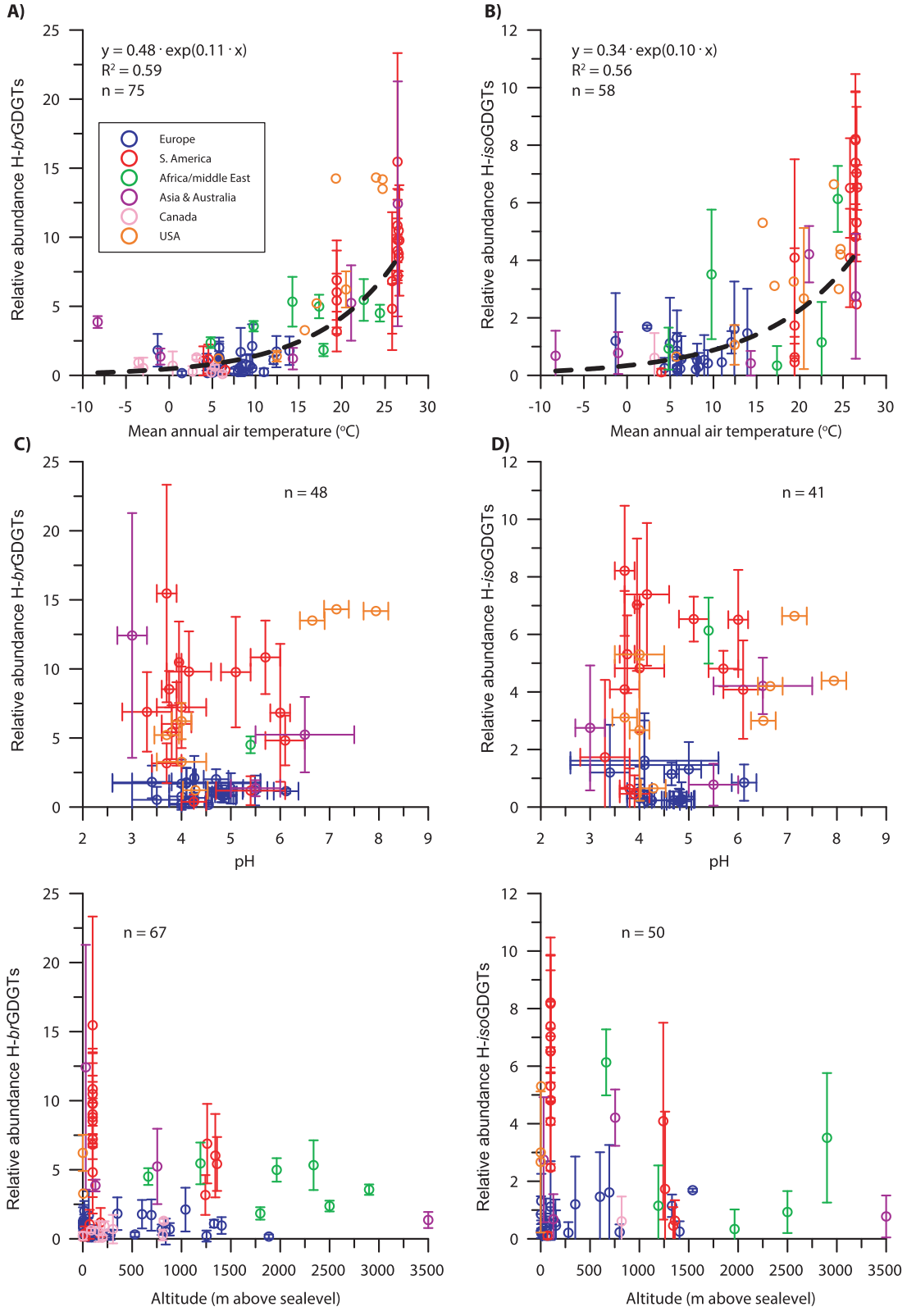

Fig. 5. Relative abundance of H-*br*GDGTs (left) and H-*iso*GDGTs (right) over regular GDGTs for each of the peatlands versus mean annual air temperature (A and B), pH (C and D), and altitude (E and F). Note that the average for each peatland is plotted and only values with a relative abundance > 0.1 are shown. Peatlands are color coded according to their region. Vertical error bars represent one standard deviation from the average for peatlands where multiple samples were analyzed. Horizontal error bars in panel C and D indicate the spread in pH reported for each peatland. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

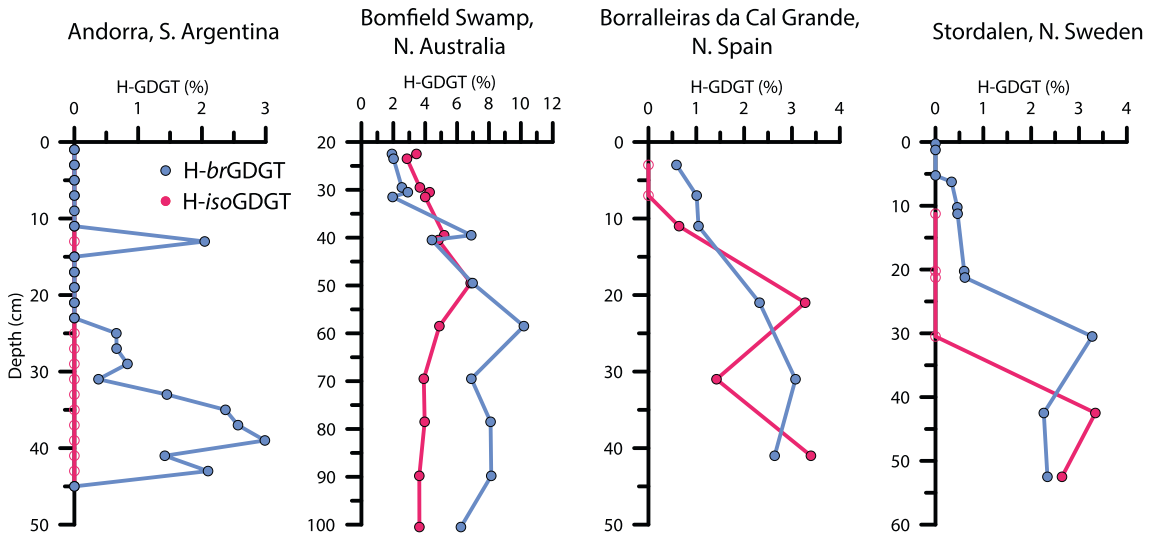

Fig. 6. Downcore relative abundance of H-*br*GDGTs and H-*iso*GDGTs over regular GDGTs in four peatlands; Andorra (Argentina), Bomfield Swamp (Australia), Borralleiras da Cal Grande (Spain), and Stordalen (Sweden); Site details available in (Burrows et al., 2014; Chambers et al., 2014; Pontevedra-Pombal et al., 2013; Swindles et al., 2015).

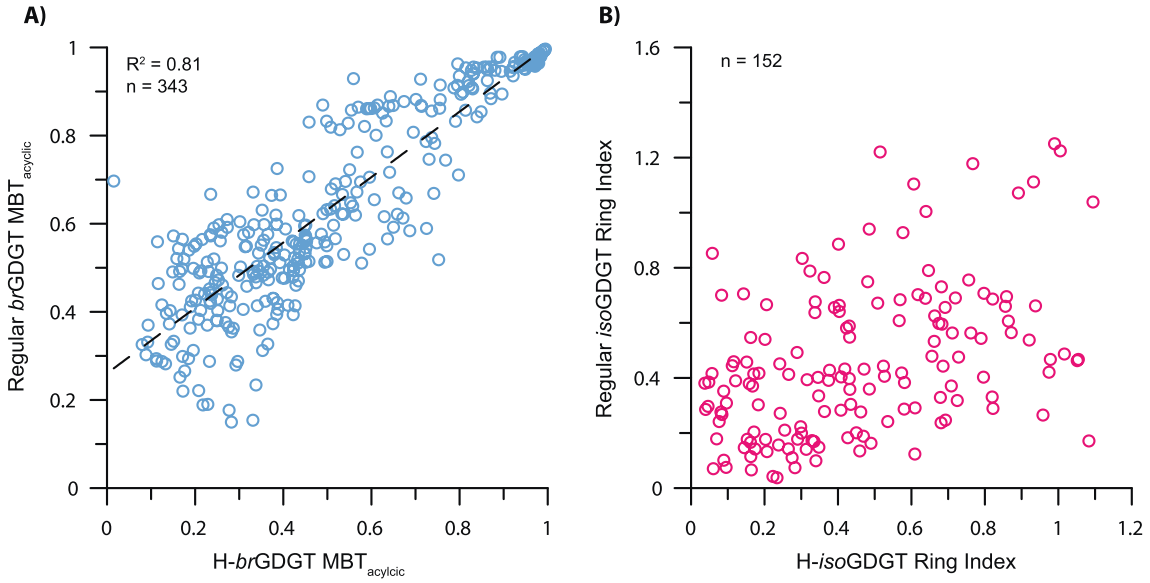

Fig. 7. Comparison between the degree of methylation of acyclic regular and H-*br*GDGTs (A) and comparison of the ring index of regular and H-*iso*GDGTs (B).

and pH (Fig. 5c and d). Even within one climatic zone, e.g. only peats from subtropical climates with MAAT > 20 °C (not shown), there is no clear correlation. These findings are consistent with previous findings from terrestrial hot springs (Jia et al., 2014), which suggested no clear correlation between the relative abundance of H-*iso*GDGTs and pH over a wide pH range (2–10). The lack of correlation between H-GDGTs and pH is surprising. For example, if the formation of an extra covalent bond between the two alkyl chains (H-GDGTs) is used to enhance membrane stability, it would be expected that peats with low pH are characterized by a higher relative abundance of H-GDGTs. However, we do not observe this relationship in our dataset.

4.3. Correlation with temperature

Our results suggest a positive correlation between the relative abundance of H-GDGTs and temperature (Fig. 5a and b). However, there is significant scatter that indicates that other factors influence the relative abundance of H-GDGTs. For example, some peats from Scotland

(MAAT = ~6 °C) have a higher relative abundance of H-*iso*GDGTs compared to those found in some of the Brazilian peats (MAAT = ~19 °C).

Despite this, the relative abundance of H-*br*GDGTs over regular *br*GDGTs only exceeds 10% in tropical peats with MAAT > 19 °C. H-*iso*GDGTs also generally occur in higher relative abundances in the tropics. We previously showed that the degree of methylation of *br*GDGTs, reflected in the methylation of 5-methyl branched tetraethers (MBT'_{5me}) index, in peat is linearly correlated with MAAT (Naafs et al., 2017b), similar to that previously observed in mineral soils (De Jonge et al., 2014a; Naafs et al., 2017a; Weijers et al., 2007). A comparison between the degree of methylation of regular *br*GDGTs with no cyclopentane moieties, $MBT_{acyclic}$ (Eq. (3)), and the degree of methylation of H-*br*GDGTs (H-$MBT_{acyclic}$: Eq. (4)), demonstrates coherency (Fig. 7) and adds to the growing evidence for a strong temperature control on the wider *br*GDGT distribution in peat. Similarly, the correlation between the degree of methylation of regular and H-*br*GDGTs suggests that H-*br*GDGTs might be produced by the same group of organisms, potentially acidobacteria (Sinninghe Damsté et al., 2014, 2011; Weijers et al., 2006a).

Previous studies using regular *iso*- and *br*GDGTs have applied linear, logarithmic or even sigmoidal relationships (e.g., Kim et al., 2010; Liu et al., 2009) to interrogate relationships between distributions and environmental variables. Currently, there is insufficient understanding of the mechanistic underpinning of GDGT distributions to justify one relationship over another; as such, the relative strength of empirical relationships has frequently been the foundation for finding the optimal correlation. Although there is significant scatter for both *br*- and *iso*GDGTs, an exponential relationship best describes the correlation with temperature with a coefficient of correlation (r^2) of 0.59 and 0.56 (p-value <0.01)), respectively. The coefficients of correlation (r^2) are slightly higher for the linear correlations (0.64 and 0.58, respectively), but the residual mean squares are also much higher for the linear correlations. Nonetheless, given the current lack of mechanistic understanding and the scatter in our data, we are reluctant to propose a definitive mathematical relationship between temperature and the relative abundance of H-GDGTs, although we do note that our data provide strong evidence that such a relationship exists. A temperature relationship is supported by evidence from (deep) marine sediments, where the relative abundance of H-*iso*GDGTs is correlated with temperature across a range of thermal gradients (Sollich et al., 2017).

However, these findings are partly inconsistent with previous work from terrestrial hot springs (Jia et al., 2014), which suggest no correlation between the relative abundance of H-*iso*GDGTs and temperature (range 20–95 °C). We cannot explain these contradictory results, but it is likely that the community of archaea is different between thermophilic hot springs and mesophilic peat. This is consistent with Jia et al. (2014), who that argued that the archaeal community differed between different hot springs used in their study.

Although it is unclear which archaea are producing H-*iso*GDGTs in our peats, H-*iso*GDGTs have previously been identified in *Methanothermus fervidus* (Morii et al., 1998), *Aciduliprofundum boonei* (Schouten et al., 2008a), different strains of *Thermococcales* (Sugai et al., 2004), *Ignisphaera aggregans* (Knappy et al., 2011), and *Methanopyrus kandleri* (Liu et al., 2012). Of these, *M. fervidus* and *M. kandleri* are methanogens. As methanogens are particularly abundant in peat, we tentatively suggest that (uncultured) relatives of these types of *Euryarchaeota* could be the source of H-*iso*GDGTs in our peat samples. However, future studies should explore whether these types of methanogens are abundant in peatlands.

Crucially, the relative abundance of H-*iso*GDGTs in hot springs, hydrothermal vents, and extremophilic cultures is much higher (up to 50%) than that encountered in peats (up to 11%) and marine sediments (<10%) of different ages (Lincoln et al., 2013; Liu et al., 2012; Schouten et al., 2008b), further suggesting that H-GDGTs are produced in higher abundances at higher temperatures. Our results indicate that either GDGT-producing archaea and bacteria produce more H-GDGTs at higher temperature or that the communities shifts towards more H-GDGT producing organisms at higher temperature. There is evidence that the archaeal community in peat depends on different environmental factors (Rooney-Varga et al., 2007). For example, some cultured H-*iso*GDGT-producing archaea are methanogens and previous peat incubation studies have shown a relative increase in methanogenic archaea (e.g. *Methanosaeta*) in peat incubated at higher temperature (Hoj et al., 2007). The high relative abundance of *iso*GDGT-0 in all peat samples is consistent with an archaeal community dominated by methanogens (Koga et al., 1993) and molecular phylogenetic studies show that the archaeal community in peat is dominated by methanogens such as *Methanomicrobiales* and M*ethanosarcinales* (Utsumi et al., 2003). A change in the archaeal taxonomic composition towards methanogens at higher temperatures could explain the higher abundance of H-*iso*GDGTs in tropical compared to mid/high-latitude peats.

However, the similar response of both H-*iso*GDGTs and H-*br*GDGTs (i.e. across two domains of life), suggests that the temperature response represents a common physiological response. Indeed, culture data indicate an analogous response in thermophilic *Euryarchaeota*, with a shift in their lipid composition from predominantly diethers to macrocyclic diethers (e.g. "H-diethers") at higher growth temperatures (Sprott et al., 1991). Future culture experiments of H-*iso*GDGT producing archaea should be used to determine whether archaea can shift the relative contribution of H-*iso*GDGTs in response to temperature or whether there is a change in archaeal communities in response to temperature. Regardless, our results suggest that temperature exerts a control on the relative abundance of both H-*iso*GDGTs and H-*br*GDGTs in peat with highest relative abundances occurring in tropical peat.

4.4. Correlation with altitude

Previous work demonstrated that the distribution of regular *br*- and *iso*GDGTs in natural archives such as mineral soils can be correlated with altitude (e.g., Coffinet et al.,

2014; Ernst et al., 2013; Liu et al., 2013; Sinninghe Damsté et al., 2008). Although our database does not contain an altitude transect from the same region as some of the previous studies, our database does contain peats from 0 to 3500 m above sea level. When the relative abundance of H-GDGTs in peat is plotted versus altitude (Fig. 5e and f), there is no clear correlation. Although H-GDGTs are generally more abundant at lower altitudes, this is likely driven by temperature.

4.5. Downcore profiles and impact of preservation and water/oxygen content on H-GDGTs

Previous work indicates that moisture content can impact the *br*GDGT distribution in minerals soils (Dang et al., 2016). Similarly, culture experiments of archaea demonstrate that changes in oxygen content can impact the *iso*GDGT distribution (Qin et al., 2015). We do not have water or oxygen content data for individual samples. However, comparing downcore profiles across the acrotelm/catotelm boundary can provide some insights into the impact of changes in the water/oxygen content as well as the impact of preservation (age) on the H-GDGT distribution.

The downcore increase in the abundance of H-GDGTs parallels that seen previously for regular (intact) *iso*GDGTs and *br*GDGTs (Peterse et al., 2011; Weijers et al., 2004), potentially reflecting predominantly (but not necessarily exclusive) anaerobic source organisms. Intriguingly, the abundance of H-GDGTs relative to regular GDGTs also increases in some (but not all) downcore peat profiles (Fig. 6). We note that this could partly arise from analytical difficulties arising from the low overall GDGT concentration at the top of some peats, but one explanation for the change in relative abundances is preferential production of H-GDGTs at depth in the water saturated anoxic acrotelm. Alternatively, it could indicate that H-GDGTs are more resistant to degradation compared to regular GDGTs and the increase is a preservation signal. However, this hypothesis seems unlikely given evidence that GDGTs appear to be preferentially produced in the catotelm (see above) and because ether bonds of H- and regular GDGTs are proposed to be attacked first during degradation (Liu et al., 2016a). Moreover, in peat, *br*GDGT turnover times might be the highest in the partly oxic acrotelm at the top of peat (Huguet et al., 2017). If preferential degradation does influence the relative abundance of H-GDGTs relative to regular GDGTs we would expect to see the highest relative abundance of H-GDGTs at the top of peat, the opposite of our findings.

Therefore, we suggest that H-GDGTs are preferentially produced at depth, in the anoxic, water-saturated catotelm by anaerobic archaea and bacteria. This is consistent with the observation that all reported organisms that produce H-*iso*GDGTs are strict anaerobes (Knappy et al., 2011; Liu et al., 2012; Morii et al., 1998; Schouten et al., 2008a; Sugai et al., 2004). This finding is also consistent with the presence of H-*br*GDGTs in the oxygen minimum zone of the tropical Pacific (Xie et al., 2014).

4.6. Degree of cyclization of H-versus regular isoGDGTs

Although the degree of methylation of regular *br*GDGTs with no cyclopentane moieties ($MBT_{acyclic}$) and the degree of methylation of H-*br*GDGTs with no cyclopentane moieties ($H\text{-}MBT_{acyclic}$) is correlated (Fig. 7a), we did not find a clear correlation between the degree of cyclization of regular *iso*GDGTs, reflected in the ring index (Eq. (5)), and degree of cyclization of H-*iso*GDGTs (Eq. (6)) in peat (Fig. 7b). The same result is obtained if we exclude H-*iso*GDGT-0 and *iso*GDGT-0 from the ring index (not shown). There is also no correlation between the degree of cyclization of H-*iso*GDGTs (Eq. (6)) and temperature (not shown).

The lack of a correlation in degree of cyclization between regular and H-*iso*GDGTs contrasts with monospecies culture data in which the degree of cyclization of regular and H-*iso*GDGTs is correlated (Knappy et al., 2011). The observed lack of a correlation in the degree of cyclization of regular and H-*iso*GDGTs in peat could be because the capacity to produce regular *iso*GDGTs is widespread in archaea (Pearson and Ingalls, 2013; Schouten et al., 2013; Villanueva et al., 2014) and that the archaeal community in peat is large and diverse (Cadillo-Quiroz et al., 2008), while the ability to produce H-*iso*GDGTs appears to be limited to some species of *Euryarchaeota* and *Crenarchaeota*. Indeed, both taxonomic analyses (as compiled in Pearson and Ingalls, 2013; Schouten et al., 2013) and previous analyses of peat (e.g., Pancost et al., 2003) suggest that *iso*GDGT-0 has a wider range of archaeal sources than the cyclopentane-bearing *iso*GDGTs. In addition, the community composition between different peats could be very different due to difference in vegetation, temperature, pH, etc. Furthermore, comparing natural samples (with a diverse microbial community) to monospecies cultures is complicated because different archaeal strains produce different patterns of *iso*GDGT-cyclization even at the same growth temperature (e.g., Elling et al., 2015, 2017; Schouten et al., 2013).

4.7. Implications

These results provide evidence in favor of the general hypothesis (Knappy et al., 2011; Schouten et al., 2008b, 2013) that the formation of an extra covalent bond in H-GDGTs ensures membrane stability at higher temperature. Crucially we demonstrate a correlation with temperature for both H-*iso*GDGTs and H-*br*GDGTs. We have previously shown that the distribution of *br*GDGTs in peat is highly correlated to temperature (Naafs et al., 2017b). However, it is surprising that the adaptation to temperature by forming a covalent bond between the two alkyl chains is present across the "lipid divide" (Lombard et al., 2012). A similar adaptation strategy to temperature stress suggests parallel or convergent evolution (potentially facilitated by lateral gene transfer) in H-GDGT producing archaea and bacteria or might suggest that the last common ancestor had this capability. In this context, future studies should explore whether members of the deep-branching Asgard

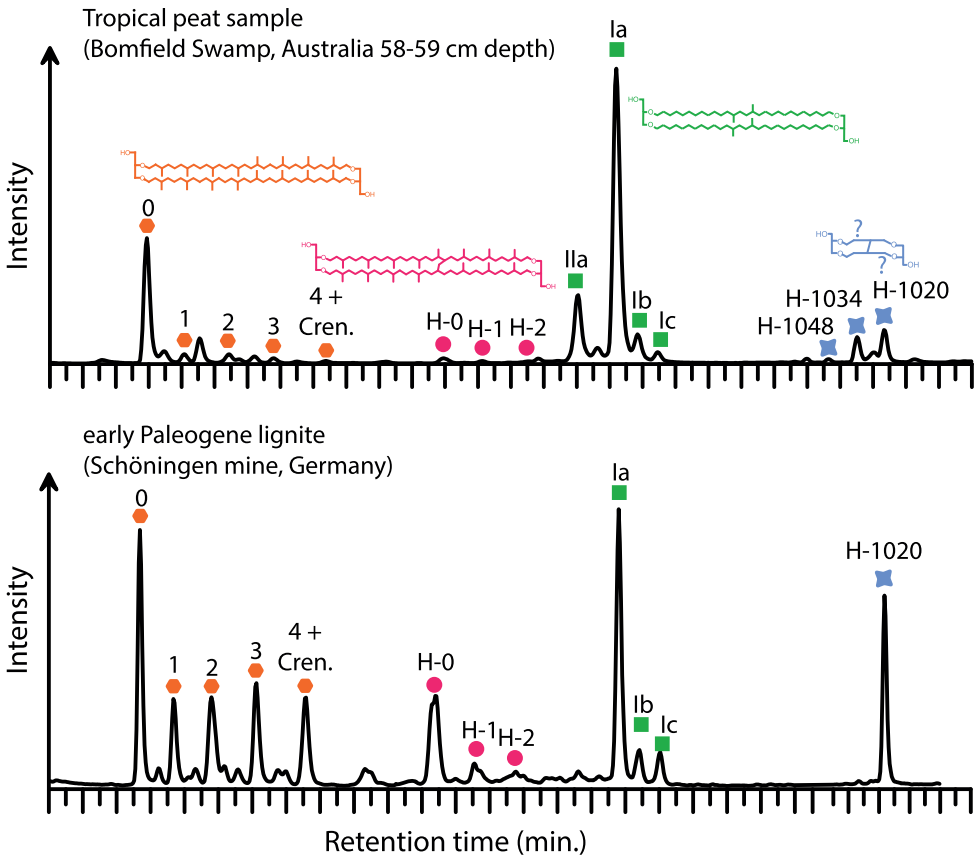

Fig. 8. HPLC-APCI-MS base peak chromatogram of an Australian tropical peat sample (top) with chromatogram of thermally immature early Paleogene lignite sample from Schöningen Seam 1 (bottom), highlighting the high relative abundance of H-GDGTs in the lignite sample.

archaea (Zaremba-Niedzwiedzka et al., 2017) have the capacity to produce H-*iso*GDGTs.

At this time, the correlation between H-GDGTs and temperature (Fig. 5) is not robust enough to be used as a quantitative palaeothermometer. However, our results do suggest that immature coal deposits (i.e. lignites) from past warm climates such as the Eocene and Paleocene should have a higher relative abundance of H-GDGTs compared to modern peats from the same latitude. To test this hypothesis we re-visited samples from Seam 1 within the Schöningen Südfeld mine, northern Germany, deposited at ~48 °N palaeolatitude (Ahrendt et al., 1995; Inglis et al., 2017; Riegel et al., 2012). Seam 1 was deposited during the latest Paleocene and/or earliest Eocene and is inferred to represent an ancient ombrotrophic bog deposit deposited under (sub)tropical conditions. (Inglis et al., 2017, 2015; Robson et al., 2015). Within Seam 1, H-*iso*- and H-*br*GDGTs are abundant with the relative abundance ranging between ca. 10 and 40%. H-*br*GDGTs are dominated by H-1020, consistent with the dominance of *br*GDGT-Ia in these samples (Fig. 8). The H-*iso*GDGTs are dominated by H-*iso*GDGT-0, consistent with the dominance of *iso*GDGT-0 over regular *iso*GDGTs in these samples.

Crucially, the relative abundances of H-GDGTs in this early Paleogene lignite are higher than found in modern-day mid-latitude peats. This is consistent with the *br*GDGT-based temperatures for these samples which are significantly higher than modern temperatures at this latitude (Inglis et al., 2017). However, for some samples the relative abundance is significantly higher than found in any modern peat, including tropical settings. We speculate that this is (at least partly) due to subsurface production of H-GDGTs under elevated burial temperature. While subsurface production may increase the relative abundance of H-GDGTs, subsurface production is unlikely to have influenced *br*GDGT-derived temperature estimates obtained from this site (see Inglis et al., 2017 for further discussion). A potential subsurface origin for H-GDGTs requires further testing, but it is consistent with the very high abundance of H-shaped tetraacids found in oils (Sutton and Rowland, 2014; Sutton et al., 2010).

5. CONCLUSIONS

We determined the relative abundance of H-GDGTs in a database of global peat samples. Contrary to previous findings, we demonstrate that both archaeal H-*iso*GDGTs and bacterial H-*br*GDGTs are abundant in terrestrial settings. In addition to known H-GDGTs, we report the presence of two new H-*br*GDGTs; H-1034 and H-1048. We demonstrate that the relative abundance of both bacterial and archaeal H-GDGTs compared to regular GDGTs is related to temperature with the highest abundance in

tropical peats. Our results support the hypothesis that H-GDGTs are used to maintain membrane stability at higher temperature. The observation that both bacterial and archaeal membrane lipids respond to temperature by adding a covalent bond indicates the same adaption across the lipid divide between these two domains of life, suggesting parallel or convergent evolution.

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